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| 13. ABSTRACT (Maximum 200 words) Fundamental studies have been conducted on the factors which determined chromophore hyperpolarizability to optical loss ratio and which determined chromophore interaction leading to attenuation of electric field poling-induced electro-optical activity. These studies have lead to a new generation of electro-optic materials exceeding for the first time the performance of inorganic electro-optic materials. Lattice hardening chemistry used to lock-in poling-induced electro-optic activity has been systematically investigated. Fundamental studies of poling-induced optical loss have been conducted. A new technique for processing polymer buried channel waveguides, multi-color photolithography, has been introduced. | | | |
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SYNTHESIS AND PROCESSING OF NEW SECOND ORDER NONLINEAR OPTICAL
MATERIALS
F49620-94-1-0201

Final Progress Report Submitted to

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REVIEW OF OBJECTIVES:

The systematic investigation of the design and synthesis of second order nonlinear optical chromophores, for significantly improved optical nonlinearity and the capability of being adapted to the fabrication of prototype electro-optic devices, is the primary objective of this program. Chromophores must not only exhibit improved optical nonlinearity relative to acentric azobenzene and stilbene chromophores but must also exhibit appropriate solubility in processing solvents, must be amenable to covalent incorporation into polymeric materials, must exhibit chemical stability under a variety of processing conditions including exposure to elevated temperatures and high electric fields, must be capable of being arranged into macroscopic noncentrosymmetric arrangements yielding large second order optical susceptibilities. A second objective is to explore new processing protocols appropriate for utilizing improved chromophores. This includes investigation of a variety of polymer lattice hardening reactions used in conjunction with induction of chromophore order by electric field poling. A third objective is to carry out a preliminary evaluation of new materials for use with reactive ion and photoprocessing of active and passive waveguide structures. A final objective is to develop polymeric materials capable of incorporating large quantities of trivalent rare earth metal ions which can be used to achieve optical amplification in polymeric optical fibers.

STATUS OF EFFORT:

Development of Improved Chromophores. A large number of chromophores with $\mu\beta$ values in excess of 1000×10^{-48} esu (i.e., 2 to 10 times that of the widely used standard DANS) have been synthesized. Molecular hyperpolarizabilities have been characterized by EFISH and hyper-Rayleigh scattering (see Dalton, et al., Chemistry of Materials, 7, 1060-1081 (1995) and Dalton, Chemistry & Industry, no. 13, 510-514, 7 July 1997). Thermal properties have been evaluated by TGA. Structural characterization has been evaluated high resolution NMR, UV-Vis, FTIR, Mass Spectroscopy and by Elemental Analysis. A program has recently been set in place to evaluate photochemical and photophysical properties of chromophores at relevant wavelengths. These chromophores have been prepared with reactive functionalities which permit incorporation into various polymer processing protocols and resulting materials have been evaluated under poling and lattice hardening conditions. Macroscopic electro-optic coefficients, measured by ellipsometry, attenuated total reflection and two-slit interference modulation, have been observed in the range 15 to 70 pm/V. The fact that high $\mu\beta$ chromophores initially (without chromophore derivatization) exhibited optical nonlinearities

(electro-optic coefficient and second harmonic generation coefficient) significantly below the values predicted by $\mu\beta$ /(molecular weight) scaling has been quantitatively explained. London theory has been extended to treat the competition of chromophore-electric field (acentric ordering) and chromophore-chromophore (acentric disordering or centric ordering) interactions. The shape of chromophores has been explicitly taken into account. Theoretical calculations quantitatively predict the variation of electro-optic coefficients which chromophore loading in polymeric matrices. In particular, electro-optic coefficients are observed to go through a maximum with chromophore loading (number density). Attenuation of acentric order is shown to be most problematic for prolate ellipsoidal chromophores. Chromophores of spherical shape are likely optimal for maximizing optical nonlinearity but theory predicts that oblate ellipsoidal chromophores should also be explored. The effects of electrical conductivity and photoconductivity on poling-induced acentric order has also been quantitatively investigated. In the process of this investigation chromophores have been identified which offer exciting new levels of photoconductivity and novel optical limiting properties. New Processing Methods. The understanding of the role played by chromophore-chromophore electrostatic interactions in influencing both achievable acentric order and lattice hardening and of the roles played by electrical conductivity and photoconductivity has dramatically influenced electric field poling protocols including the role of cladding layers in such protocols. Specifically new poling protocols, including pulsed field poling, have been introduced and have led to improved optical nonlinearity. In the pulsed field poling protocol, a periodic pulsed field of increased strength is applied, in addition to the lower strength steady state poling field, for short periods of time. The pulse periods are sufficiently short to avoid dielectric breakdown of the materials but are sufficient to disrupt chromophore-chromophore interactions. Because chromophore-chromophore interactions strengths vary dramatically with relative orientation and distance, such transient disruptions allow the steady state field-chromophore interaction to successfully compete with the chromophore-chromophore electrostatic interactions and pole the material. A detailed study of poling-induced optical loss has been carried out. Two primary contributors to such loss have been identified and are (1) surface damage (studied by SIMS) from the corona field and (2) migration of chromophores under the influence of the electric field. A detailed study of optical loss due to material heterogeneities arising during lattice hardening reactions has also been carried out. GPC has been used to investigate oligomer growth and distribution during precuring and lattice hardening. Control crosslinking reagent stoichiometry was found to be particularly critical in minimizing optical loss due to processing.

Substantial strides have also been made in the area of fabricating buried channel waveguides. The superiority of electron cyclotron resonance methods to reactive ion etching has been demonstrated. Control of reactive ion processing conditions has been shown to be relevant to reduction of optical losses in both polymeric waveguides and in the transition of light from polymeric to silica waveguides. Optical losses due to wall roughness in buried channel waveguides have been reduced to 0.01 dB/cm which is insignificant. Coupling losses due to mode mismatch at a silica to polymer waveguide junction have been reduced to less than 2 dB by a systematic investigation of tapered transitions. Polymeric Fiber Amplifiers. Rare earth ion incorporation into polymeric waveguides has been achieved exploiting oxygen and nitrogen chelation. Polymer structure modification (e.g., fluorination) has been carried out to reduce optical loss. Polymer chelates have been developed to minimize quenching of luminescence due to interaction between metal centers. Polymer structures have been controlled to permit preparation of fibers by extrusion although optical characterizations to date have largely been carried out on spin cast thin films. Most recently, a promising series of light harvesting dendrimers have been developed.

ACCOMPLISHMENTS/NEW FINDINGS:

1. Theoretically and experimentally demonstrated that the high dipole moments and large molecular polarizabilities of new high $\mu\beta$ (first hyperpolarability) chromophores lead to critically important electrostatic intermolecular interaction magnitudes which in turn dominate realizable poling efficiency and strongly influence the efficiency of lattice hardening reactions. The current failure of unmodified "high $\mu\beta$ chromophores" to be successfully translated into macroscopic electro-optic materials appropriate for device fabrication has been quantitatively explained and insight has been gained into routes appropriate for circumventing current limitations. Indeed, modification of chromophores from their current prolate ellipsoidal shapes to spherical and oblate ellipsoidal shapes appear to provide a simple route to optimizing macroscopic optical nonlinearity through more efficient noncentrosymmetric assembly. Macroscopic optical nonlinearities of a number of chromophores has been improved by factors of 2-3. Preliminary evidence has already been obtained indicating that improved lattice hardening can be realized by chromophore modification to inhibit intermolecular aggregation driven by electrostatic interactions.

The work on London theory can be considered to be a major theoretical breakthrough with relevance to a variety of materials problems including liquid crystalline and block copolymer materials.

2. The role of electrical conductivity and photoconductivity influencing realizable noncentrosymmetric order in electric field poling experiments has been elucidated. The excitation spectrum of photoconductivity has been determined for materials exhibiting large photoconductivities. Excitation across the HOMO-LUMO gap is required for photoconductivity (i.e., two photon contributions are negligible) so that electro-optic modulation operation of these materials at the communication wavelengths of 1.3 and 1.5 microns is not problematic. Photoconductivity effects can be avoided by poling in the dark. Electrical conductivity problems due to ionic contamination can be reduced by appropriate purification techniques such as chromophore recrystallization. Note that because of their large polarizability, high β chromophores may form large transfer adducts with ionic species and care must be exercised in disrupting these and removing ionic impurities.

3. The issue of optical loss due to mode mismatch between silica fiber waveguides and active polymeric electro-optic modulator waveguides has been addressed (Proc. SPIE, 3005, 65-76, 1997), with considerable success exploiting both reactive ion etching (RIE) and multi-color photolithography (MCP) techniques. Tapered transitions, which approximate the profile predicted theoretically by Marcatili (J. Lightwave Technol. 3, 386-93, 1991) for zero loss, have been fabricated and tested. Dramatically reduced coupling losses have been observed. Work on multi-color photolithography has been coordinated with RVM Scientific.

4. New "blue-shifted" high β chromophores have been synthesized for application at 980 nm. This work has been carried out in conjunction with Deacon Research/Gemfire Corporation for development of improved flat panel display technology.

5. New electrically conducting cladding materials have been developed which may facilitate the production of electro-optic devices with reduced V_p values. New photoconducting materials have been developed which may prove of utility for a variety of applications including cladding materials, photorefractive materials, reconfigurable radar, etc.

6. Further refinements have been made in the area of lattice hardening protocols. New classes of heteroaromatic nonlinear optical polymers which exhibit improved thermal stability of poling-induced optical nonlinearity have been synthesized.

7. Materials and processing protocols have been developed facilitating the vertical integration of polymeric buried channel electro-optic waveguides with VLSI semiconductor electronic circuitry. These has been achieved by the USC team of Steier and Dalton with degradation of the performance of either electro-optic or electronic circuitry.

8. Several new spectroscopic characterization techniques, including frequency-agile, multi-dimensional, multi-wave mixing, phase-sensitive-detection nonlinearity spectroscopy and new techniques for measuring electro-optic coefficients, have been developed.

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INTERACTIONS/TRANSITIONS :

INVITED LECTURES:

1. Third International Conference on Frontiers of Polymers and Advanced Materials, Kuala Lumpur
2. 28th Organosilicon Symposium, Gainesville, Florida
3. 1995 ACS/PMSE Symposium on Polymeric Organic Materials: Solid State Properties and Smart Materials, Anaheim, California
4. Materials Research Society Symposium on Thin Films for Integrated Optics Applications, San Francisco, California
5. National Technology Transfer Center, Technology Applications Review, Orlando, Florida
6. NASA Lecturer, Fifty Fourth Frontiers in Chemistry Lecture Series, Cleveland, Ohio
7. NATO Advanced Research Workshop on Photoactive Organic Materials: Science and Applications, Avignon, France
8. SPIE International Symposium on Nonlinear Optical Properties of Organic Materials VIII, San Diego, California
9. SPIE International Symposium of Optical and Photonic Applications of Electroactive and Conducting Polymers, San Diego, California

10. SPIE International Symposium on Fullerenes and Photonics II, San Diego, California
11. Symposium on Optoelectronic Materials and Conjugated Polymers, IV International Conference on Advanced Materials, Cancun, Mexico
12. 7th International Conference on Unconventional Photoactive Systems, Stanford, California
13. OSA/ACS Organic Thin Films for Photonics Applications, Portland, Oregon
14. International Business Communications Conference on Commercial Applications for Organo Electronic Materials, Mariana del Rey, CA
15. Society of Plastics Engineers (SPE) annual technical meeting ANTEC, Indianapolis, IN
16. American Chemical Society National Meeting, New Orleans, LA
17. American Chemical Society National Meeting, Orlando, FL
18. SPIE International Symposium on Fullerenes and Photonics III, Denver, CO.
19. ACS/OSA Symposium on Organic Thin Films for Photonic Applications, Orlando, Florida
20. International Conference on Nonlinear Optics 3, Marco Island, Florida
21. Fourth International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt
22. Symposium on Dendrimers and Hyperbranched Polymers, Spring American Physical Society National Meeting, Kansas City, Mo.
23. National Meeting, ANTEC, Society of Plastics Engineers, Toronto, Canada
24. AFOSR/ONR Photonic and Electro-Optic Polymer Review, Atlantic Beach, Florida
25. Sino-American Topical Meeting and Exhibit, Solid State Lasers: Materials and Applications, Tianjin, People's Republic of China
26. Gordon Conference on Organic Thin Films, Salve Regina
27. The International Society of Optical Engineering 42nd Annual Meeting, San Diego, CA.

INVITED SEMINARS :

Numerous seminars at various industries, government laboratories, and universities including seminars at University of Florida, University of Illinois, University of Washington, NASA Marshall Space Flight Center, University of California at Los Angeles, the Max-Planck-Institut fur Polymerforschung (Mainz FRG) and the Optical Science Center of the University of Arizona.

Presentations were also made before the Board of Gemfire Corporation, senior management of Hughes Research Laboratories, the Board of the Loker Hydrocarbon Research Institute and the Board of Trustees of the University of Southern California, etc.

CONSULTATIVE AND ADVISORY PANEL SERVICE :

1. Bule Ribbon (Final Phase) Panel for the Selection of Presidential Faculty Fellows (National Science Foundation)
2. Consultant, Medical Research Service, Veterans Administration
3. Materials Research Science & Engineering Center Panel, National Science Foundation
4. Panel 15, Office of Energy Efficiency and Renewable Energy Photovoltaics Review, U.S. Department of Energy
5. Advisory Comittee, National Institutes of Health Biomedical Technology Centers at the University of Illinois and at Dartmouth University
6. Consultant, Arizona Disease Control Research Commission, State of Arizona
7. Immunobiology Study Section, National Institutes of Health
8. Advisory Committe, The New York Herman F. Mark Institute for Polymers Science and Engineering at the Polytechnic University, NY, NY
9. Editorial Advisory Board, Chemistry of Materials, American Chemical Society
10. Consultant, Princeton Materials Research Center.

INTERACTIONS AND TRANSITIONS :

Research Interactions and Technology Transitions include EniChem/ROI Tech/Lightwave Microsystems Corp. (A. Jen/J. Kenney), Cal Tech/JPL (S. Marder and J. Perry), Hughes Research Laboratory (U. Efron), TACAN/Integrated Photonics Technology, Ipitek (Y. Shi), AdTech (S. Sinha), Deacon Research/Gemfire (W. Bischel), RVM Scientific (R. Mustacich), IBM (D. Burland), Physical Optics Corporation (G. Savant), and Thermax Systems, Inc. (Bruce Sangster), Radiant Research, Inc (B. Davies and R. Chen).

NLO active polymeric films were provided to TACAN/Ipitek, RVM Scientific, Deacon Research/Gemfire and Physical Optics Corporation to permit these organizations to pursue evaluation of these materials for phototype device development. TACAN and POC are interested in low frequency, low cost modulator fabrication. TACAN is interested in evaluating the long term, in-field performance of polymeric electro-optic modulators. RVM Scientific is interested in using new photolithographic

techniques to fabricate low loss waveguides and low loss transitions from polymer waveguides to silica fiber transmission lines. Deacon Research is interested in fabricating full color, flat panel displays from polymeric electro-optic modulators.

Photoactive chromophores were transitioned to Hughes Research Laboratory for use in development of high density optical memories.

Thermax Systems, Inc. Is interested in using photoactive chromophores in cooling applications.

Discussions have been held with Exxon, Allied Signal and Audemars Corporations and with NASA Marschall Space Flight Center who have expressed interest in collaborating and participating in technology transfer.

INVENTIONS:

None

HONORS/AWARDS

1. The 1996 Richard C. Tolman of the American Chemical Society (April 23,1997)
2. Paul C. Cross Endowed Lectureship in Chemistry, University of Washington, Seattle, WA, May 29, 1996
3. NASA Lecuturer, 54th Frontiers of Chemistry Lecture Series, Case Western Reserve University, Cleveland, OH, April 27, 1995.
4. Harold and Lillian Moulton Distinguished Professorship of Chemistry (Endowed Chair), University of Southern California
5. Scientific Co-Director of the Loker Hydrocarbon Research Institute, University of Southern California
6. Nominated for the National Academy of Science
7. Nominated for the Chemistry of Materials Award of the American Chemical Society

The research has been featured in the news articles in the following publications: The Baltimore Sun newspaper, Chemical & Engineering News, Research & Development Magazine, Laser World Focus, Business Week, Science, Wired Magazine, Photonics Spectra, Chemistry & Industry, Polymer Science News, Photonics Science News, Ind. Eng. Chem. Res., etc. A television episode of "Strange Universe" will focus on the research; the filming was completed recently at the Loker Hydrocarbon Research Institute. The research has been featured on two occasions on local radio broadcasts.

Note: Mr. Aaron Harper was the first recipient of the American Chemical Society Organic Division Fellowship. Mr. Harper is now an Assistant Professor of Chemistry at Texas A&M University.